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Lila M. Mulloth and John E. Finn

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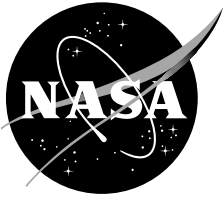
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SUMMARY

Carbon dioxide adsorption data were obtained for a 5A zeolite manufactured by AlliedSignal Inc. (Des Plaines, Illinois). The material is planned for use in the Carbon Dioxide Removal Assembly (CDRA) for U.S. elements of the International Space Station. The family of adsorption isotherms covers a temperature range of 0° to 250°C, and a pressure range of 0.001 to 800 torr. Coefficients of the Toth equation are fit to the data. Isothermic heats of adsorption are derived from the equilibrium loading data.

INTRODUCTION

The Carbon Dioxide Removal Assemblies (CDRA) to be operated in U.S. segments of the International Space Station will use an adsorption-based device known as a “four-bed molecular sieve,” or 4BMS, to remove excess carbon dioxide exhaled by the crew and onboard animals (ref. 1). This device, shown schematically in figure 1, uses a packed bed filled with a solid sorbent media (5A zeolite) to scrub CO₂ from the air blown through it. The bed becomes saturated with CO₂ during operation and is regenerated several times a day on a programmed cycle. During the regeneration cycle, the process air stream is diverted to a second (and previously regenerated) CO₂-scrubbing bed, while heat and vacuum are used to remove concentrated carbon dioxide from the bed being regenerated.

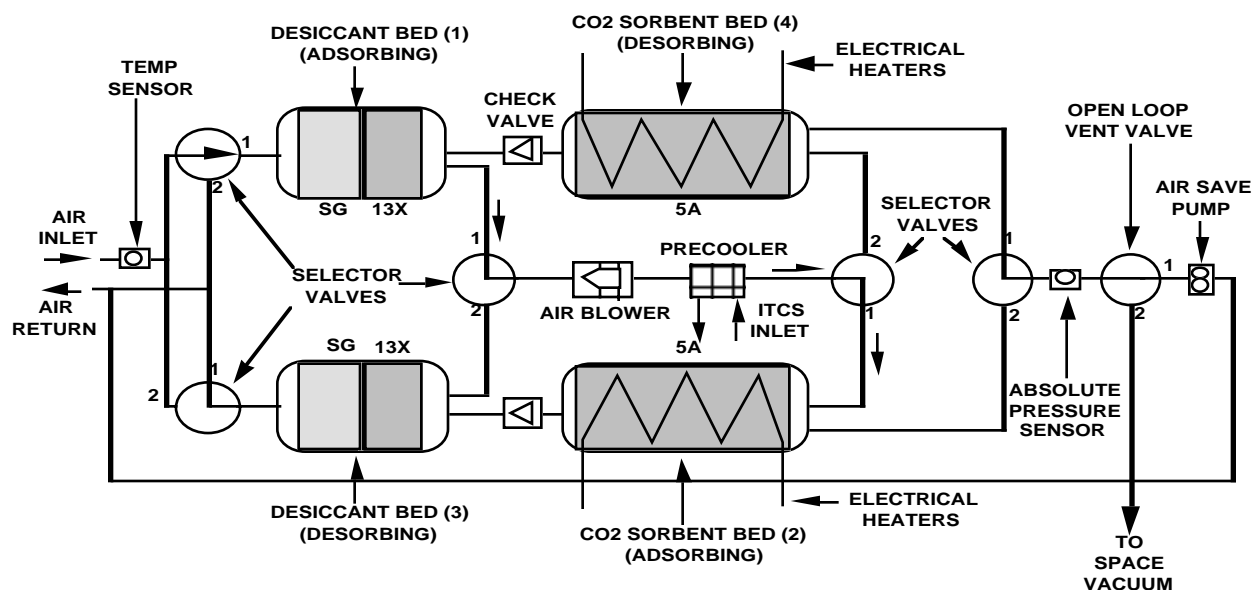


Figure 1. Schematic of the “four-bed molecular sieve” unit planned for use in CDRA’s in U.S. elements of the International Space Station (ref. 2). The CO₂-scrubbing 5A zeolite beds are located in the center of the figure.

Mathematical modeling and simulation of the 4BMS unit is useful for efficient optimization of its cycle times and operational parameters. The modeling effort, performed at NASA Marshall Space Center, requires accurate adsorption data over a range of temperatures and gas concentrations. The collection and presentation of this data is the subject of this document, and represents an update to previously collected data (see for example, ref. 3).

This report summarizes the results of adsorption equilibrium experiments performed on a sample of the CO₂ sorbent media (ASRT 5A, manufactured by AlliedSignal, Inc.) that is currently planned for use in flight. Single component isotherms were obtained at temperatures of 0°, 25°, 50°, 75°, 100°, 175°, and 250°C over a pressure range of approximately 0.001 to 800 torr.

EXPERIMENTS

Apparatus

Single component adsorption isotherm experiments were performed on an apparatus based on a common static volumetric procedure (see for example, ref. 4). Briefly, the apparatus works as follows (see fig. 2): a quantity of the adsorptive gas is introduced into a manifold of precisely known volume and is held at a constant temperature. The pressure of this gas is measured, allowing precise calculation of the number of moles of the gas in the chamber through a gas law. The sorbent sample, held in an independent constant temperature bath, is then exposed to this gas and the system is allowed to equilibrate. Finally, the sorbent is again isolated, and the final number of moles of adsorptive gas in the manifold is calculated. The change in the quantity of adsorbed gas can be calculated from the change in the amount of gas in the manifold after exposure to the sorbent, after appropriate corrections are made for sample cell volume and temperature.

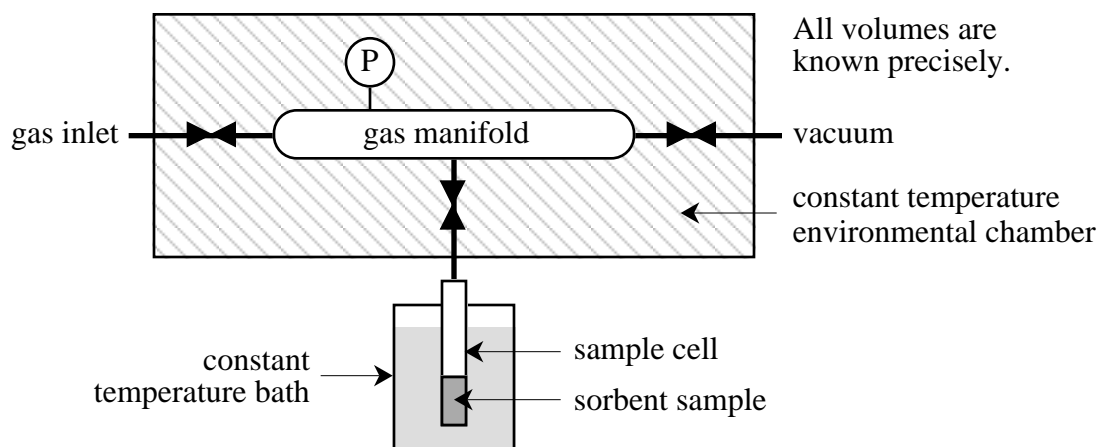


Figure 2. Schematic of apparatus used for measuring single component adsorption equilibria.

High accuracy is obtained in this apparatus through careful measurements of volumes, pressures, and temperatures, and through maintaining a low leak rate. Volumes are known to within 0.01%, pressures to 0.15%, and temperatures to 0.1 °C (0.04% and better for these experiments). The helium leak rate of the system is approximately 1×10^{-7} cc·atm/sec.

Materials

The sample of ASRT 5A zeolite sorbent was provided by NASA Marshall Space Flight Center. It has the form of light beige, brittle, cylindrical pellets approximately 1/16-inch diameter and roughly 1/8-inch long. The gas used in the experiments was 99.99% pure CO₂, obtained from Matheson Gas Products, Inc.

Procedure

Approximately one gram of sorbent sample was used for each experiment. Samples were prepared by placing them under a trickle flow of helium at 320°C. The cell containing the sorbent sample was connected to the system, and the free space of the sample cell at the temperature of the experiment was determined using helium. The system was then evacuated at 150°C until no outgassing of helium from the sample was observed.

Experiments performed at 0°C used water-ice in the constant temperature bath. Experiments at 25°, 50°, and 75°C used an automatically controlled constant temperature water bath. Experiments at 100°C and higher used an automatically controlled fluidized sand bath.

The criterion for equilibrium for the experiment was 0.1% change in pressure over a period of 5 minutes. Time needed for equilibration varied from 10 to 30 minutes depending on the pressure. Data points were obtained sequentially, from low to higher pressures, in a single run. Initial points required longer equilibration times than points obtained later in the run.

DATA

A family of CO₂ adsorption isotherms for ASRT 5A from 0° to 250°C is shown in figure 3. The raw data are tabulated in the Appendix. Coefficients of the Toth equation (ref. 5)

$$q = mP(b + P^t)^{-1/t} \quad (1)$$

where q is quantity adsorbed, P is pressure, and m , b , and t are adjustable constants, were fit to the data; these curve fits are shown as lines on figure 3. The Toth coefficients for the seven isotherms are also tabulated in the Appendix.

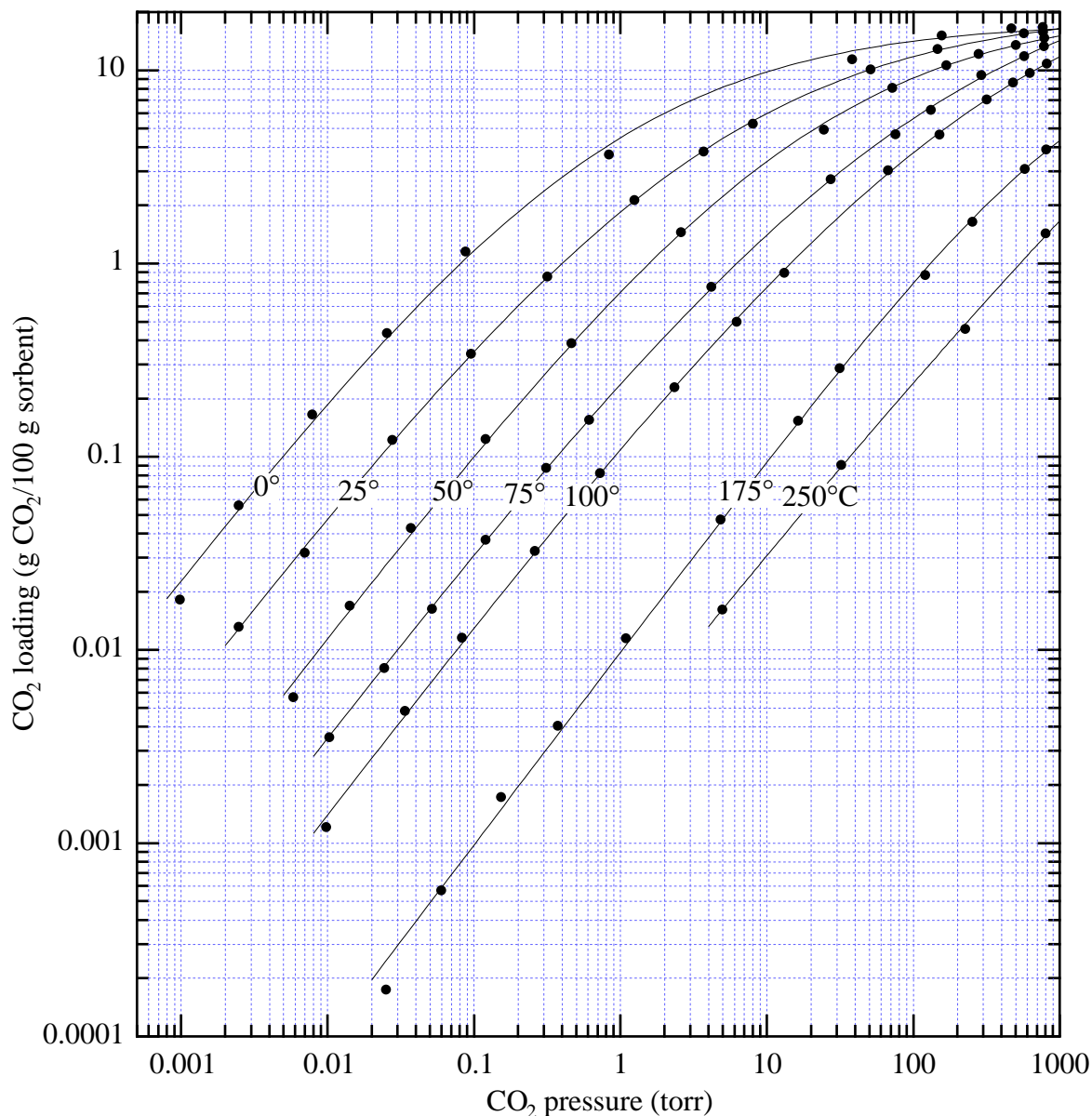


Figure 3. CO₂ adsorption equilibrium isotherms for ASRT 5A from 0° to 250°C. Toth equation fits to the data are shown as lines.

The isosteric heat of adsorption required for the energy balance in a flow system, can be determined as a function of loading by obtaining the slopes of plots of $\ln P$ versus reciprocal absolute temperature at constant loading (ref. 6). Figure 4 illustrates these plots for a wide range of loadings, using the Toth equation to interpolate between data points; there is generally excellent linearity. Figure 5 shows the isosteric heats obtained from the slopes of these lines. The limit of the isosteric heat at zero loading, 44.9 kJ/mol, is in good agreement with a figure of 45.2 kJ/mol reported by Ruthven (ref. 7).

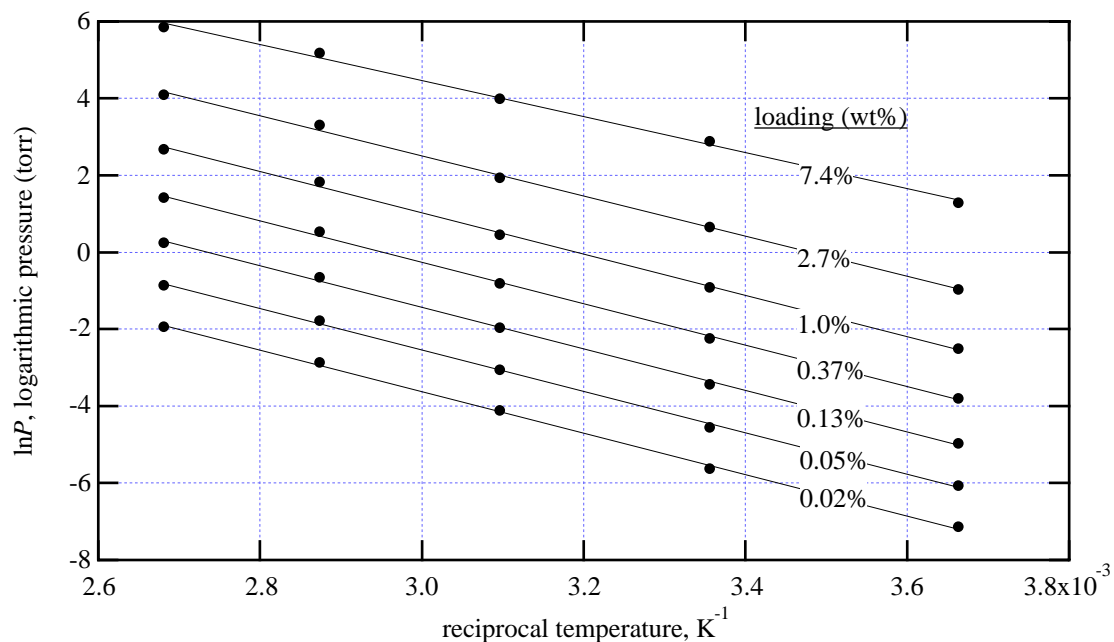


Figure 4. Plots of $\ln P$ versus reciprocal absolute temperature for loadings ranging from 0.02 to 7.4 weight percent. Isosteric heat as a function of loading calculated from the slopes.

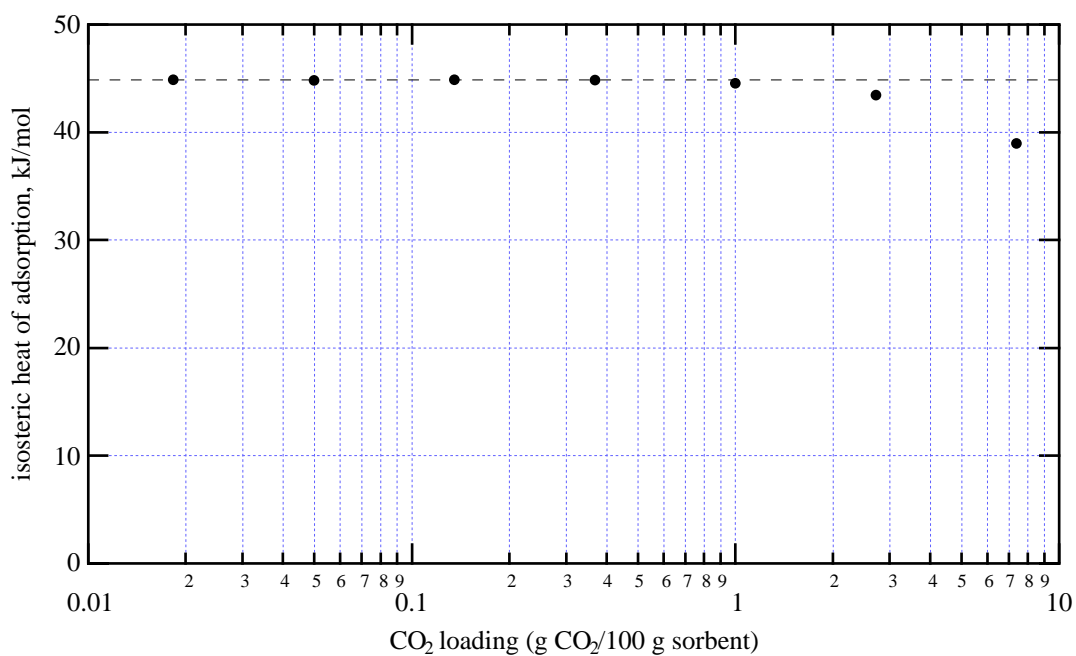


Figure 5. Isosteric heats calculated at various loadings from the isotherm data shown in figure 3. The dashed line is the intercept in the limit of zero loading; calculated here to be 44.9 kJ/mol.

CONCLUSION

Adsorption equilibrium isotherms were obtained for the system CO₂–ASRT 5A zeolite over the temperature range 0° to 250°C for the purpose of supporting modeling of the Carbon Dioxide Removal Assembly for the International Space Station. The data are fit well by the Toth equation. Isothermic heats of adsorption were derived from the equilibrium loading data, and the heat of adsorption in the limit of zero loading agrees well with previously published results for another CO₂–5A zeolite system.

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APPENDIX

Tabulated adsorption data for CO₂ on ASRT 5A, with fitted Toth equation parameters (see equation 1 in the text) are presented below. Toth parameters have units consistent with torr for pressure and weight % for loading. Note that these coefficients are valid only for interpolation of data (especially for the higher temperature isotherms).

0°C

pressure (torr)	loading (wt%)
0.00098	0.0182
0.00248	0.0560
0.00785	0.165
0.0254	0.437
0.0873	1.15
0.834	3.67
38.1	11.4
156	15.2
467	16.5
763	16.8
Toth coefficients, units of torr, wt%	
m	17.867
b	0.853206
t	0.444986

25°C

pressure (torr)	loading (wt%)
0.00247	0.0132
0.00699	0.0318
0.0277	0.122
0.0952	0.341
0.316	0.855
1.24	2.13
3.70	3.79
8.00	5.28
51.1	10.1
146	12.9
569	15.5
768	15.8
Toth coefficients, units of torr, wt%	
m	20.8173
b	1.66122
t	0.403689

50°C

pressure (torr)	loading (wt%)
0.00583	0.00570
0.0142	0.0169
0.0371	0.0428
0.120	0.124
0.462	0.386
2.59	1.45
24.5	4.94
72.0	8.13
168	10.6
279	12.1
500	13.5
784	14.7
Toth coefficients, units of torr, wt%	
m	20.9923
b	3.56105
t	0.447872

75°C

pressure (torr)	loading (wt%)
0.0102	0.00354
0.0244	0.00806
0.0515	0.0163
0.120	0.0371
0.310	0.0876
0.610	0.156
4.16	0.759
27.2	2.73
75.5	4.67
132	6.24
292	9.45
572	11.8
780	13.3
Toth coefficients, units of torr, wt%	
m	39.939
b	5.23465
t	0.356774

100°C

pressure (torr)	loading (wt%)
0.00979	0.00121
0.0338	0.00483
0.0827	0.0116
0.260	0.0325
0.725	0.0822
2.34	0.229
6.24	0.500
13.1	0.895
67.3	3.04
151	4.64
317	7.06
478	8.64
622	9.68
815	10.8
Toth coefficients, units of torr, wt%	
m	45.9782
b	8.23681
t	0.367554

175°C

pressure (torr)	loading (wt%)
0.0250	0.000175
0.0596	0.000569
0.153	0.00173
0.374	0.00405
1.09	0.0115
4.82	0.0472
16.3	0.154
31.4	0.286
120	0.873
252	1.65
575	3.08
806	3.89
Toth coefficients, units of torr, wt%	
m	15.5414
b	141.673
t	0.672267

250°C

pressure (torr)	loading (wt%)
4.98	0.0162
32.2	0.0906
226	0.459
799	1.43
Toth coefficients, units of torr, wt%	
m	6125.71
b	16.8625
t	0.20097

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE November 1998		3. REPORT TYPE AND DATES COVERED Technical Memorandum
4. TITLE AND SUBTITLE Carbon Dioxide Adsorption on a 5A Zeolite Designed for CO ₂ Removal in Spacecraft Cabins			5. FUNDING NUMBERS	
6. AUTHOR(S) Lila M. Mulloth* and John E. Finn				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Ames Research Center * Lockheed Martin Moffett Field, CA 94035-1000 Moffett Field, CA 94035-1000			8. PERFORMING ORGANIZATION REPORT NUMBER A9800125	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, DC 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA/TM-1998-208752	
11. SUPPLEMENTARY NOTES Point of Contact: John E. Finn, Ames Research Center, MS 239-15, Moffett Field, CA 94035-1000 (650) 604-1028				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified-Unlimited Subject Category – 25 Availability: NASA CASI (301) 621-0390			12b. DISTRIBUTION CODE Distribution: Standard	
13. ABSTRACT (Maximum 200 words) Carbon dioxide adsorption data were obtained for a 5A zeolite manufactured by AlliedSignal Inc. (Des Plaines, Illinois). The material is planned for use in the Carbon Dioxide Removal Assembly (CDRA) for U.S. elements of the International Space Station. The family of adsorption isotherms covers a temperature range of 0° to 250°C, and a pressure range of 0.001 to 800 torr. Coefficients of the Toth equation are fit to the data. Isothermic heats of adsorption are derived from the equilibrium loading data.				
14. SUBJECT TERMS Carbon dioxide removal, Air revitalization, Carbon dioxide adsorption			15. NUMBER OF PAGES 14	
			16. PRICE CODE A03	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT	